

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification <sup>6</sup> : A23D 9/05, C11B 15/00</p>	<p>A1</p>	<p>(11) International Publication Number: <b>WO 97/37546</b> (43) International Publication Date: 16 October 1997 (16.10.97)</p>
<p>(21) International Application Number: PCT/EP97/00829 (22) International Filing Date: 19 February 1997 (19.02.97) (30) Priority Data: 96302539.0 11 April 1996 (11.04.96) EP (34) Countries for which the regional or international application was filed: GB et al. (71) Applicant (for all designated States except US): LODERS CROKLAAN B.V. [NL/NL]; Zaandijkerweg 36, NL-1521 AX Wormerveer (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): CAIN, Frederick, William [GB/NL]; Loders Croklaan B.V., Zaandijkerweg 36, NL-1521 AX Wormerveer (NL). DEKKER, Willem [NL/NL]; Loders Croklaan B.V., Zaandijkerweg 36, NL-1521 AX Wormerveer (NL). MOORE, Stephen, Raymond [GB/GB]; Unilever Research Colworth Lab., Colworth House, Sharnbrook, Bedfordshire MK41 1LQ (GB). (74) Agent: UNILEVER N.V.; Patent Division, P.O. Box 137, NL-3130 AC Vlaardingen (NL).</p>		<p>(81) Designated States: CA, JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  Published With international search report.</p>
<p>(54) Title: FREE FLOWING FAT COMPOSITIONS (57) Abstract  Free flowing fat compositions with high levels of triglycerides, containing long chain poly unsaturated fatty acids comprise: (1) a blend of fats (A) and (B) in a weight ratio 90:10 to 10:90; (2) 0-95 wt.% of a filler material, wherein fat A is a fat with <math>\geq 0.5</math> wt.% of LC PUFA'S and fat B is a hard fat, while the composition fulfills the requirement that: [N<sub>30</sub>(unstab) of fat (A) or the blend + % of filler in composition] <math>\geq 70</math>.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

Free flowing fat compositions

Free flowing fat compositions are commercially available. In some of these commercially available compositions 10-20 wt % of a natural fish oil is present. In order to make these compositions free flowing a support material, such as a starch or a sugar must be present as well and even then these compositions could not contain more than 25 wt % of the fish oil(s). Therefore, these compositions had a limited use, as they do provide on the one hand the advantages of being free flowing, they also had the disadvantage that only a limited amount of fish oil could be added by using them in e.g. food products. Therefore, there existed a great demand for free flowing fat compositions with which also higher dosages of polyunsaturated triglycerides, such as fish oil or conjugated linoleic acids (= CLA's) could be added upon its use.

According to WO 94/00146 marine oils are blended with solid fats in such a way that the marine oils become part of the crystalline structure of the solid fat. This blend is applied in liquid state to porous pellets of undefined nature, followed by cooling and crystallisation of the fat. Examples of the solid fat are tempered rapeseed oil, monoglycerides, diglycerides or mixes thereof. The product is applied as fodder for aquatic organisms.

From JP 07/133491 it is known to prepare oil soluble substances containing solid materials by adding a liquid oil soluble substance to silica gel and solidifying it. The liquid oil soluble substance includes poly unsaturated fatty acid compounds. The compositions according to this disclosure have the disadvantage that relatively high amounts of an inorganic filler material (= silica gel) have to be present in the compositions, which makes them less useful in food compositions. Moreover we found that the amount of fish oil that could be incorporated in compositions that were free flowing was rather limited. In JP 03/269096 it is disclosed that fluid compositions

that contain oils such as fish oil or hardened fish oil can be obtained if they are blended with 20-70 wt % of flour, in particular soybean flour. So again these products require the presence of a filler material. The presence of  
5 such a filler is not always appreciated in food products. In that instance this document does not reveal a solution for compositions that are free flowing, contain relatively high amounts of fish oil but that do not contain a filler material. Also in EP 425 213 free flowing compositions are  
10 disclosed that require the presence of filler materials such as starch or caseinate.

We found that the presence of a hard fat in our compositions provided us with compositions that contain high amounts of poly unsaturated fats, are still free  
15 flowing and do not require the presence of a filler. It should be understood that a filler material can be present as well, however the hard fat should also be present in that instance.

Therefore we found that by applying a hard fat in  
20 combination with the long chain polyunsaturated triglycerides, with or without a filler (or support) material, compositions could be obtained that were free flowing and which would enable us to add higher dosages (ie at least 10 wt%) of long chain polyunsaturated  
25 triglycerides.

Therefore, our invention concerns a free flowing fat composition comprising:

- (i) a blend of fats (A) and (B) in a weight ratio of  
30 90:10 to 10:90

(ii) 0-95 wt % of a filler material

wherein fat A is a fat with at least 0.5 wt % of long chain polyunsaturated fatty acids, preferably being w-3 fatty acids or conjugated linoleic acids and fat B is a hard fat, so that  $N_{50}$  (unstab) of the fat (A) or the blend + % filler in composition] is at least 70, preferably at least 75, in particular 80-160.

10 Above compositions have a number of benefits over known compositions:

- (1) using above composition can avoid the introduction of non lipid materials in the systems, wherein they are applied.
- 15 (2) higher concentrations of long chain PUFA materials can be achieved in free flowing products.
- (3) the products display excellent dispersibility in cold water.
- (4) the products have a particle size distribution which makes them most suitable for use in e.g. infant formula.

In order to be able to add higher amounts of the long chain polyunsaturated fatty acids, we prefer to use a fat A, that contains more than 2 wt %, preferably 4-50 wt % and most preferably 5-20 wt % of these LCPUFA's.

Suitably a fat blend is used that displays an  $N_{50} > 25$ , preferably  $> 35$  more preferably 40-80, and in particular 45-75.

30

It is mentioned here that N-values refer to solid fat contents, measured by NMR pulse techniques on unstabilized fats. Unstabilized meaning that the fat was melted at 80°C, kept at 60°C for 5 minutes, cooled to 0°C and kept at 0°C for 1 hour and kept at measurement temperature for 30 minutes.

Although in the absence of a filler free flowing compositions could be made, containing 10-25 wt % of the fat, comprising the long chain polyunsaturated triglycerides, it was also found that the level of these latter (soft) fats could be increased to about 35 wt % if a filler was present in the composition. The amount of filler material could vary from 2.5-90 wt %, preferably 10-80 wt%, most preferably 15-70 wt %.

10 Suitable filler materials are selected from the group, consisting of: sugars, such as glucose, fructose or sucrose, flour, cocoa powder, coffee powder, coffee granules, whey powder, skim milk powder, butter milk powder, food grade inorganic solid powders, such as silica, 15 alumina, titania and zirconia.

The ratio, wherein fats A and B can be applied can range from 10-90 wt %, most preferably 20-80 wt % for fat A to 90-10 wt %, most preferably 80-20 wt % for fat B.

20

The hard fat can be selected from a wide range of hard fats, such as hardened oils or stearin fractions of vegetable fats. Application of fats B with a melting point of more than 35°C, preferably more than 45°C, in particular 25 more 50-80°C however lead to the best results.

Examples of such hard fats B are triglycerides, diglycerides, monoglyceride or a mixture thereof, in particular selected from palm oil stearin, hardened soybean 30 oil mpt 65°C, hardened sunflower oil mpt 65°C, distearin, monostearin, monopalmitin.

Our free flowing fats are characterized by a particle size distribution (by sieving) of 5-500  $\mu\text{m}$ , preferably 10-250 35  $\mu\text{m}$ , most preferably 20-200  $\mu\text{m}$ . Bigger particle than 500  $\mu\text{m}$  mean that lumps are present, that give problems during dispersion of the composition upon its use.

Examples of fats that can be applied as fats A are fats that comprise at least two different long chain PUFA's  $L_1$  and  $L_2$ , in particular being present in a ratio of  $L_1 : L_2 > 2$ , preferably  $> 3$ . Examples of such fats are disclosed in  
5 our copending applications EP 95302942.8, EP 95302843.6, EP 95302944.4 and EP 95308228.6.

Particular examples of such fats A are derived from natural fish oil, modified fish oil, fish oil concentrate,  
10 fractionated fish oil, enzymically treated fish oil or oils from microbial sources. Other examples of fats A are triglycerides, containing conjugated linoleic acids.

Examples of sources for CLA's can be found in :  
US.5.430.066, US.5.428.072, US.5.070.104, US.5.017.614,  
15 US.5.208.356, or EP 411.011

Fats can be made from these CLA's by enzymic or chemical conversions thereof. From above fats we prefer to use these fats, wherein two different LCPUFA's are present in a ratio of at least 2, preferably at least 3.

20

Part of our invention are also food products, comprising at least a fat, wherein the fat is present in the form of the free flowing composition according to claims 1-11.

25 Examples of these food products are: bread; bakery goods; such as cakes, pastries or, croissants; infant formula; creamers; coffee whiteners.

The free flowing composition can be made by blending of  
30 fats A and B, after which the blend is cryomilled, spray-crystallized or spray-dried. Cryomilling in the presence of solid  $CO_2$  or liquid  $N_2$  being the most preferred routes. Cryomilling being performed in a mill in the presence of a low temperature agent, such as solid  $CO_2$ . As a mill any  
35 known type of mill can be used, suitable for use at low temperature.

EXAMPLESI. Using a fish oil

As fish oil a semi-refined tuna oil was applied, containing 30.9 wt% of polyunsaturated fatty acid moieties (mainly DHA and EPA). As hard fat hardened soybean oil mpt 65°C was applied. As filler material either sugar or flour was used. The free flowing character of the product was evaluated by a panel. It was expressed by a number varying from 1-5 (1 = bad, 5 = very good).

The fish oil or the blend of fish oil and hard fat were mixed with about equal weight amounts of solid CO<sub>2</sub> and milled in a turmix-blender for 1-5 min.

Thereafter, if appropriate a filler material was added in the amounts indicated in the table.

II. Using conjugated linoleic acid (= CLA)

Example I was repeated. However CLA was applied in stead of fish oil. The composition used comprised 31 wt% free CLA; 13 wt% hardened bean oil 65 and 65 wt% sugar. The mixture obtained scored a free flowing of 4.

Table

N <sub>30</sub> (blend)	%FH in blend	level of filler	free flowing character
42	60	-	not cryomillable *
52	50	-	ibid *
63	40	0	1 *
72	30	0	4
81	20	0	5
72	30	50 % sugar	5
52	50	50 % sugar	5
32	70	50 % sugar	3
35	67	25 % sugar	2 *
72	71	30 % sugar	4
72	30	50 wt % flour	5
52	50	50 wt % flour	5
32	70	50 wt % flour	3
35	67	25 wt % flour	1 *
0	100	65 wt % sugar	2 *
0	100	50 wt % sugar	1 *

\* = Not according the invention

CLAIMS

1. Free flowing fat composition comprising:
  - (i) a fat blend of fats (A) and (B) in a weight ratio of 90:10 to 10:90 and
  - (ii) 0-95 wt % of a filler materialwherein fat A is a fat with at least 0.5 wt % of long chain polyunsaturated fatty acids, preferably being w-3 fatty acids or conjugated linoleic acids and fat B is a hard fat, so that  $[N_{30} \text{ (unstab)} \text{ of the blend} + \% \text{ filler in composition}]$  is at least 70, preferably at least 75, in particular 80-160.
2. Free flowing composition according to claim 1, wherein the content of long chain polyunsaturated fatty acids in fat A is more than 2 wt %, preferably 4-50 wt %, in particular 5-20 wt %.
3. Free flowing composition, according to claims 1-2, wherein the fat blend (A) + (B) displays an  $N_{30} > 25$ , preferably  $> 35$ , more preferably 40-80, in particular 45-75.
4. Free flowing composition, according to claims 1-3, wherein the content of filler material is 2.5-90 wt %, preferably 10-80 wt %, in particular 15-70 wt %.
5. Free flowing composition, according to claims 1-4, wherein the filler material is at least one component, selected from the group consisting of: sugars, such as glucose, fructose or sucrose, flour, cocoa powder, coffee powder, coffee granules, whey powder, skim milk powder, butter milk powder, food grade inorganic solid powders, such as silica, alumina, titania and zirconia

6. Free flowing composition according to claims 1-5, wherein the fat blend comprises 20-80 wt % of fat A, containing the long chain polyunsaturated fatty acids and 80-20 wt % of the hard fat B.
7. Free flowing composition according to claim 6, wherein hard fat B has a melting point of more than 35°C, preferably more than 45°C, in particular 50-90°C.
8. Free flowing composition according to claim 6, wherein fat A is derived from fish oil, modified fish oil, fish oil concentrate, fractionated fish oil, enzymically treated fish oil or oils from microbial sources.
9. Free flowing composition according to claims 1-8, wherein hard fat B is a triglyceride, diglyceride, monoglyceride or a mixture thereof, in particular selected from palm oil stearin, hardened soybean oil mpt 65°C, hardened sunflower oil mpt 65°C, distearin, monostearin, monopalmitin.
10. Free flowing composition according to claims 1-9, wherein the composition has a particle size distribution (by sieving) of 5-500 µm, preferably 10-250 µm, most preferably 20-200 µm.
11. Free flowing composition according to claim 8, wherein fat A comprises at least two different long chain polyunsaturated fatty acids  $L_1$  and  $L_2$ , which are present in a ratio  $L_1 : L_2 > 2$ , preferably  $> 3$ .
12. Food product, comprising at least a fat, wherein the fat is present in the form of the free flowing composition according to claims 1-11.

13. Food product according to claim 12, wherein the food product is selected from the group, consisting of:  
bread; bakery goods; such as cakes, pastries or croissants; infant formula; creamers; and coffee whiteners.
14. Process for the preparation of a free flowing composition, according to claims 1-11, wherein a blend is made of fats A and B, which blend is cryomilled, spray-crystallized or spray-dried.

# INTERNATIONAL SEARCH REPORT

International Application No  
PLI/EP 97/00829

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 A23D9/05 C11B15/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 A23D C11B A23L A21D A23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 9529 Derwent Publications Ltd., London, GB; AN 95-220934 XP002012870 & JP 07 133 491 A (YONEDA K) , 23 May 1995 cited in the application see abstract	1,2,4,5, 10,12
Y	---	6-9
Y	DATABASE WPI Week 8810 Derwent Publications Ltd., London, GB; AN 88-068369 XP002012871 & JP 63 023 736 A (MEIJI MILK PRODS KK) , 1 February 1988 see abstract ---	6-9
-/-		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- \* "A" document defining the general state of the art which is not considered to be of particular relevance
- \* "E" earlier document but published on or after the international filing date
- \* "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \* "O" document referring to an oral disclosure, use, exhibition or other means
- \* "P" document published prior to the international filing date but later than the priority date claimed

\* "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\* "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\* "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\* "&" document member of the same patent family

Date of the actual completion of the international search

6 May 1997

Date of mailing of the international search report

16. 05. 97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+ 31-70) 340-3016

Authorized officer

Dekeirel, M

# INTERNATIONAL SEARCH REPORT

International Application No.

PLI/EP 97/00829

## C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI  Week 9203  Derwent Publications Ltd., London, GB;  AN 92-020326  XP002012872  &amp; JP 03 269 096 A (NISSHIN FLOUR MILL KK)  , 29 November 1991  cited in the application  see abstract</p> <p style="text-align: center;">---</p>	<p>1,2,  4-10,12</p>
A	<p>EP 0 425 213 A (UNILEVER) 2 May 1991  cited in the application  see column 2, line 53 - column 3, line 2  see claims 1,7,8,12-14,24,25</p> <p style="text-align: center;">---</p>	<p>1,2,4,12</p>
A	<p>GB 1 164 462 A (INTERFETT  SPECIALFETTPRODUKTE) 17 September 1969  see page 1, line 16 - line 46  see page 2, line 38 - page 3, line 19  see claims 1-3</p> <p style="text-align: center;">---</p>	<p>1,4,5,12</p>
A	<p>US 4 952 224 A (LOUIS LILAKOS) 28 August  1990  see the whole document</p> <p style="text-align: center;">---</p>	<p>1,4,5,12</p>
A	<p>EP 0 643 916 A (UNILEVER) 22 March 1995  see page 2, line 18 - line 49</p> <p style="text-align: center;">---</p>	<p>1,12,14</p>
A	<p>EP 0 601 965 A (FUISZ TECHNOLOGIES) 15  June 1994  see page 3, line 36 - page 4, line 13  see claims 1,3,4,7</p> <p style="text-align: center;">---</p>	<p>1,10</p>
P,A	<p>EP 0 739 589 A (LODERS CROKLAAN BV) 30  October 1996  cited in the application  see page 3, line 26 - page 4, line 22  see claims 1,8-14</p> <p style="text-align: center;">-----</p>	<p>1,12,13</p>

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 97/00829

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 425213 A	02-05-91	CA 2028213 A	24-04-91
GB 1164462 A	17-09-69	BE 686090 A	01-02-67
		CH 456010 A	
		DE 1692523 A	05-01-72
		GB 1165320 A	24-09-69
		NL 6612083 A	28-02-67
		SE 324947 B	15-06-70
US 4952224 A	28-08-90	AU 628507 B	17-09-92
		AU 5253990 A	18-10-90
		CA 1328571 A	19-04-94
		DE 69019874 D	13-07-95
		DE 69019874 T	12-10-95
		EP 0393963 A	24-10-90
		JP 2293038 A	04-12-90
EP 643916 A	22-03-95	NONE	
EP 601965 A	15-06-94	US 5380473 A	10-01-95
		AU 670625 B	25-07-96
		AU 4917093 A	05-05-94
		CA 2108832 A	24-04-94
		JP 7308564 A	28-11-95
		PL 300831 A	16-05-94
EP 0739589 A	30-10-96	JP 8311485 A	26-11-96